

## 14. The Dynamic Radical Pair in Zero Field.

The triplet geminate radical pair produced in the primary photochemical step 2 of figure 27 is not a static structure but, because of its diffusional and rotational dynamics, constitutes a **dynamic** system and therefore is termed a **dynamic radical pair**. We need to analyze the dynamics of the pair at three levels: (1) the level of molecular dynamics whereby the partners of the pairs may be collision partners in a solvent cage or be separated by one or more solvent molecules and may interconvert between these situations; (2) the level of spin dynamics whereby intersystem crossing and rephasing of spin occur; (3) the level of chemical dynamics whereby the partners of the pair undergo chemical reactions through bond formation, scavenging or radical pair rearrangements or fragmentations. In order to keep this riot of molecular dynamic activity organized in our minds in physical space, spin space and time, we resort to a combination of energy surfaces, the vector model and conventional molecular structures. Effectively in exploring with our imaginations we need the same tools as when we explore an unfamiliar territory: a map, a clock and a compass. The map is the energy surface (molecular structures are the geographical identifiers on the map), the clock is the time scale on which the interactive dynamics occur and the compass is the magnetic field that tell us about spin orientation.

### Electronic Energy Surfaces and Molecular Dynamics.

We need to keep track of the several interacting dynamic events that are occurring simultaneously in the primary photochemical step of Figure 27, i.e., the  ${}^3\text{ACO-B} \rightarrow {}^3\text{ACO} \cdot \cdot \text{B}$  process. We start by considering an energy surface description of the process (Figure 31). The triplet surface is shown as decreasing in energy and the singlet surface as increasing in energy as the carbon carbon bond stretches and then breaks. The energy gap between the triplet and singlet states is considered to be due to the exchange interaction,  $J$ . When the bond is broken and the partners of the pair separate by a solvent molecule or two, the exchange interaction is expected to decrease to negligibly small values, so that the singlet and triplet surfaces are effectively degenerate and no longer change in energy with further separation. A representative point is shown moving down the surface (At zero field, the  $S_1 \rightarrow T_1$  intersystem crossing is assumed to have occurred to a specific triplet sublevel,  $T_z$ . We will return to this point when we consider the ESR of the radical pair).

### Definition of Terms for Radical Pairs

In order to understand the behavior of the representative point we must consider its molecular, spin and chemical dynamics as it moves along the triplet surface. Let us consider each of these dynamics separately and start with the

molecular dynamics which are represented schematically at the bottom of Figure 31. We shall employ the following terms to describe the molecular dynamics and structures of the pair.

1. **Geminate radical pairs.** A radical pair whose fragments are "born together" and share the parentage of a common precursor molecule, e.g., step 2 of figure 27.
2. **Free radicals or random radicals.** Radicals which have separated to a distance for which non-geminate reaction with radicals has a higher probability than geminate reaction.
3. **Random (or free radical) pairs.** A radical pair formed by an encounter of two free or random radicals. As one tracks the representative point as it makes an excursion down a dissociative triplet surface starting from the parent triplet excited state ( $^3R$ ) all the way to a separation of radicals that is so large that the pair becomes statistically distributed in space with radicals from other dissociations (right of Figure 31). Such a radical "pair" no longer is geminate in the sense that it becomes more probable that reencounters will occur with radicals from other dissociations than with the original geminate partner. At this point each partner of the original geminate pair is considered a "free radical" or a "random radical".
4. **Solvent cage.** The first shell of solvent molecules which surround a molecule or a radical pair (geminate or random). A pair in a solvent cage undergoes repeated collisions before one of the partners can find a "hole" in the cage wall and become separated by a solvent molecule.
4. **Contact radical pair.** A radical pair (geminate or random) whose partners are in a solvent cage without a solvent molecule between them, i.e., the pair is in contact through repeated collisions. A contact pair is able to react to form molecules through combination reactions directly if it is in the singlet state and the partners of the pair can achieve the appropriate geometry and energy required for reaction. A contact pair in the triplet state is inert to combination reactions because of Wigner's spin conservation rule for elementary chemical reactions.
5. **Solvent separated radical pair.** A radical pair (geminate or random) whose partners are separated by one or more solvent molecules.

**Visualization of the Primary Photochemical Step:  $^3ACO-B \rightarrow ^3ACO \cdot \cdot B$  in Zero Field. The Dynamic Radical Pair.**

Imagine the behavior of the representative point during the primary photochemical bond cleavage,  ${}^3\text{ACO-B} \rightarrow {}^3\text{ACO}\cdot + \cdot\text{B}$ , in zero field. The point begins to move along the triplet surface as the bond stretched and eventually breaks (Figure 31). Immediately after the bond has broken, the radical pair is produced as colliding neighbors that are born together in a solvent cage (termed the **primary, geminate collisional pair**, step (1) bottom of Figure 31). As the result of random thermally induced motions (the molecular dynamics), the partners of the pair eventually diffuse apart out of the solvent cage (producing a **geminate, solvent separated pair**, step (2) Figure 31, bottom). The solvent separated pairs make random excursions in space and time. Some of the excursions (step 3a in Figure 31, bottom) cause the geminate pair to return to the contact state in a solvent cage (such excursions are termed **reencounters** and such pairs are termed **secondary, geminate collisional pairs**). Some of the excursions lead to separation of the partners of the pair to distances so large (step 3b in Figure 31) that further diffusional trajectories (step 4 in Figure 31) are more likely to have each partner randomly encounter radicals other than the geminate partner (pair that encounter to form contact pair from such excursions are termed **random, collisional pairs**).

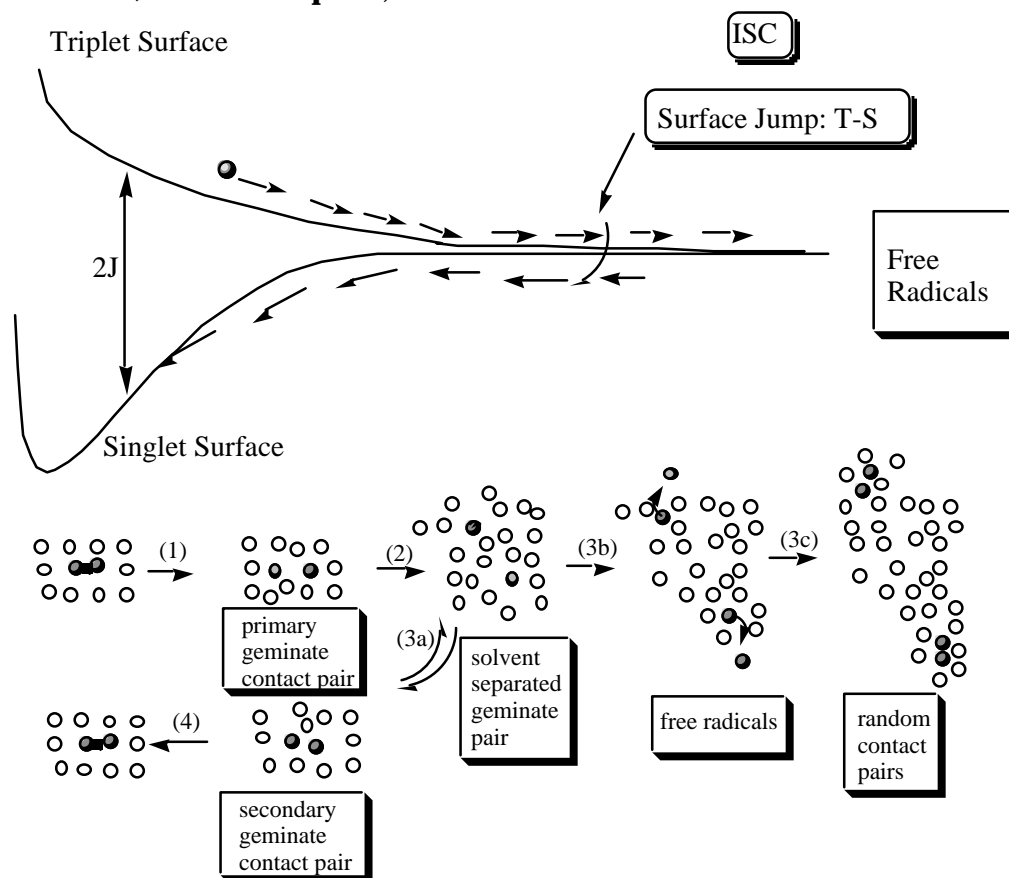


Figure 31. Surface energy diagram displaying the spin and molecular dynamic features of a dynamic radical pair.

The importance of the dynamic model of a radical pair to spin chemistry derives readily from consideration of the behavior of the triplet electronic energy surface on which the radical pair is created and the singlet electronic energy surface which the pair must reach in order to become reactive as a pair. As is shown in the top half of Figure 31, the energy separating the triplet and singlet surface is a strong function of the distance of separation of the pair in physical space. This is due to the fact that the exchange interaction,  $J$ , which is the most important contributor to the energy gap between the S and T surfaces, falls off exponentially as the electrons in the bond being cleaved are separated in physical space. **When  $J$  is large compared to available magnetic couplings, it controls the correlated precessional motion of the two odd electron spins of the pair in spin space.**

It is only during the trajectories when the pair is not in contact that intersystem crossing is important, because only under these circumstance can the electron spin experience torques that are effective enough to cause a rephasing ( $S-T_0$ ) or spin flip ( $S-T_{\pm}$ ), i.e., it is essentially only during the excursions out of the collisional state that ISC can be induced by the weak magnetic interactions available to induce reorientation or rephasing of the electron spins of the pair, because only for large excursions does the value of  $J$  decrease to values close to zero. It is our goal to be able to move fluently from a conventional structural description of the pair through a representative point on an electronic energy surface to one which simultaneously considers the dynamics of the vectors in spin space and the molecular dynamics in physical space of the solvent.

### **Regions of Magnetic Interactions for a Triplet Electronic Excited State and a Triplet Radical Pair in Zero Field**

Consider the breaking of a carbon-carbon bond in an  $\alpha$ -cleavage reaction of a triplet ketone. Figure 32 depicts a representative point moving down the triplet surface as the bond breaks. What are the regions for which the point can "jump" from the triplet surface to the singlet surface? Let us consider four regions along the energy surface at which the ISC might occur: (1) a region for which the bond is strongly stretched, but not quite broken; (2) a region for which the bond is completely broken and a contact, collisional pair in a solvent cage is produced; (3) a region for which the pair has separated by at least one solvent molecules; and (4) a region for which the pair is separated to such large distances that the geminate character is lost, i.e., the probability of reaction of random pairs is much greater than the probability of reaction of geminate pairs.

### **Visualization the Spin Dynamics. Intersystem Crossing in Geminate Radical Pairs in Zero Field.**

In the previous sections we have considered the simultaneous visualization of the motion of the representative point along energy surfaces and the molecular dynamics of the diffusional motion of the radical pair after the bond breaks. We now seek to visualize, in zero field, the spin dynamics simultaneous with conventional chemical structures of the pair, which are shown at the bottom of Figure 32. A vector model representation of the triplet is shown on the upper surface and a possible  $T_+$ -S ISC is shown (Recall that  $S_1 \leftrightarrow T_z \leftrightarrow T_+$  pathway is expected for the cleavage of the ketone triplet). The vector representation shows initial strong coupling of the two individual spin vectors in  $T_+$ . This representation means that the two spins are phase and orientation correlated and precess precisely in step. The chemical structure corresponding to this vector representation has the orbitals of the two radicals of the pair overlapping strongly and because of the overlap, strong electron exchange (large  $J$ ) occurs. We now consider the plausibility of ISC in the various regions of the energy surface explored by the representative point. We must recall that we are dealing with a dynamic representative point for the system that can only move on the triplet or singlet energy surface.

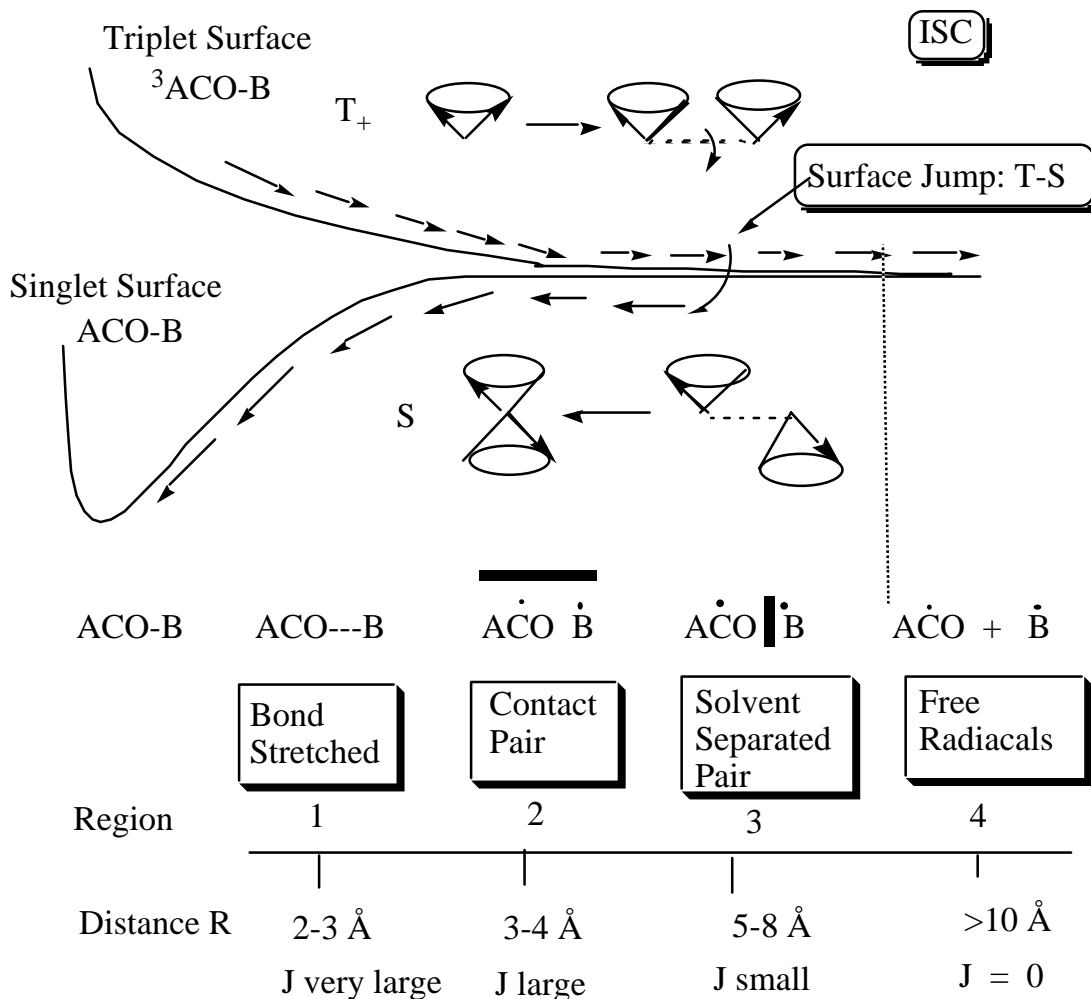


Figure 32. Distance dependence of spin correlated radical pairs. See text for discussion.

### The Bond Breaking Step. $T_+ \rightarrow {}^3RP$

In the primary cleavage step,  $T_+ \rightarrow {}^3RP$  to form  $ACO \cdot \cdot B$  (**region 1**, Figure 31,  $ca < 3 \text{ \AA}$  separation of the partners of the pair), the carbon carbon bond is stretched and then eventually broken. Is ISC plausible during the bond breaking step? The answer is, generally it is not plausible because the act of bond breaking (the time it takes the representative point to "fly through" region 1) takes of the order of a vibrational time period ( $10^{-13}$  s) whereas the rate of spin precession in organic molecules is of the order of  $10^{-10}$  s. Thus, the spin vectors are "frozen" in spin space during the time period in which the bond is broken, i.e., the orientation and phase of the spin vectors are identical as the representative point passes through region 1. This conclusion is equivalent to **Wigner's spin selection rule which says that in any elementary step of bond making or bond breaking, the spin state of the reactant and product must be**

**identical.** This situation may be viewed as a "horizontal" Franck-Condon selection rule for the spin vector: horizontal displacements on a dissociative energy surface occur faster than changes in the angular displacement of the spin vectors, thus, spin orientation is preserved when a bond breaks on a dissociative surface. Just as the Franck-Condon Principle is based on inability of nuclei motion to follow electronic reorganization when an electronic transition occurs, the Wigner Principle is based on the inability of spin motion to follow electronic reorganization when a bond is made or broken. As in the conventional Franck-Condon Principle, for which nuclear configuration is preserved upon rapid vertical jumps of the representative point, Wigner version, spin configuration (orientation or phase) is conserved upon rapid horizontal jumps of the representative point.

In addition to the kinetic problem associated with ISC in region 1, there is a second problem associated with coupling magnetic moments of the spins to induce ISC. The value of  $J$  is expected to be much larger than any available magnetic interaction for the pair, so that the coupling required for ISC is implausible. Thus, from both the kinetic standpoint and the coupling standpoint, *ISC is considered as implausible in region 1* and this conclusion is incorporated into our working paradigm of the dynamic radical pair.

### **Trajectories of the Dynamic Radical Pair.**

Figure 32 schematically displays three regions of importance (regions 2, 3 and 4 of Figure 32) to the dynamic radical pair. In **region 2** (ca  $< 4\text{\AA}$  separation), the value of  $J$  is still expected to be much larger than any available magnetic interaction for the pair, so that ISC will be inhibited. Thus, contact radical pairs experience large values of  $J$  compared to magnetic interactions because the singlet and triplet are split in energy and do not mix; the pair behaves as a spin 1 system, and ISC is difficult. We say that in the contact state the electron spins are strongly correlated. Although we conclude that ISC is implausible when the pair is in the contact state, the kinetic problem of rapid and irreversible passage through region 1 is not present. As a result, if the contact state is particularly long lived or if an exceptionally strong magnetic mixing is available to the pair, ISC may result. However, as a rule in a non-viscous solvent for typical organic radicals, *the paradigm assumes that ISC is implausible in the contact pair. (region 2)*

The solvent separated radical pair experiences a rapidly diminishing exchange interaction, which is expected to falloff exponentially (Eq. 22) in value with separation of the spins. In **region 3** (ca  $5\text{-}8\text{\AA}$  separation) the value of  $J$  is expected to be comparable to the available magnetic interactions for the pair, so that ISC is plausible. We say that for the solvent separated pair the electron spins are weakly correlated. By weakly correlated we mean that the two electron

spins, although correlated, begin to behave as if there were independent doublets. If the pair jumps from the T surface to the S surface, the molecular dynamics may either carry the singlet solvent separated pair toward a reencounter (3a in Figure 32) or toward the formation of random radicals (3b  $\emptyset$  4) in Figure 32. Thus, depending on the trajectory followed, either a geminate cage reaction or free radical formation will occur.

In **region 4** the electron correlation is 0 ( $J = 0$ ) because of the large separation between the unpaired electrons. In Figure 32 the spins are shown as correlated up to a certain point (dotted vertical line) and beyond this distance the pair is separated so far that the exchange interaction can be considered to be zero. Thus, beyond this point the magnetic interactions are so weak that the pair is considered as uncorrelated. Hypothetically, if there were no different magnetic interactions experienced by either spin, then the phase and orientational features of the initial triplet would be preserved even at infinite distances of separation! However, it is more likely that weak magnetic interactions which are not dependent on the separation of the radicals, such as electron spin-lattice coupling, electron spin orbital coupling and electron spin-nuclear hyperfine coupling, will cause the spins to lose the phase and orientational correlation imposed by the exchange interaction. In this region the pair is not well represented as a singlet or triplet, but as a pair of doublets, i.e., neither the phase nor the orientation of the spin on one center influences the phase or orientation of the the spin at the other center.

### **Order of Magnitude Estimates of ISC.**

We can obtain some insight to the magnitude required for magnetic effects to uncouple the exchange interaction and allow ISC by considering the relationship between the precessional rate,  $\omega$  (in units of rad/s), and the exchange energy,  $J$  (in units of gauss, G). The rate of precessional motion of the electron spins that are coupled by the exchange coupling is given by eq. 30, which is analogous in form to Eqs. 12 and 13.

$$\omega_{\text{ex}} = 2J/\hbar \quad (30)$$

From various modeling of organic radical pairs the value of  $J$  falls off roughly exponentially as a function of separation of the radical pairs. An approximate expression for this function is  $J \sim 10^{10}10^{-R}$ , where the units of separation are  $\text{\AA}$  and the units of  $J$  are in G. This, means that the following relationships hold for the four regions of Figure 31: Region 1,  $J \sim 10^{12}$  G; region 2,  $J \sim 10^{8-9}$  G; region 3,  $J \sim 10^2$  G; region 4,  $J \sim 0$  G. We can compare these values of  $J$  to the magnitude of hyperfine couplings of typical organic radicals (100 G) and it is clear that only in region 3 is ISC plausible, unless some exceptionally strong coupling or very long



lifetime is available in region 2. We can also compare these estimates to the value of a the magnetic field of 1,000 G (of the order of typical ESR spectrometers). We note that the applied field will control the spin motion of solvent separated (weakly correlate) geminate pairs and free radicals, but not contact pairs. Let us now consider the influence of application of a high field on spin chemistry and then consider the magnetic resonance spectroscopy of the pair in the three resgions of the energy surface.